Indian J. Phys. 54B, 88-94 (1980)

Far infrared generation in chalcopyrite crystals

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Abstract. Phase-matched difference-mixing of two close frequency lasers in nonlinear crystals is considered to generate tunable far infrared (FIR) radiation. The crystal anomalous dispersion is utilised for phase matching and the available crystal birefringence for tuning purpose. The chalcopyrite crystals are characterised by high nonlinearity and many of them show wide FIR transmission range While their visible refractive index data are available, the corresponding FIR indices are evaluated from the reflectivity data. Analysis shows that while forward wave mixing is permitted over a wide range for the studied seven II-IV-V_2 and seven I-III-VI_2 crystals, the backward mixing is possible over a wide tuning range only for $ZnSiP_2$, $CdSiP_2$ and $AgGaS_2$.

1. Introduction

Chalcopyrite crystals are important for application in nonlinear optical devices in the near and medium infrared region. It is mainly because of their reasonably high nonlinearity efficient tunable lasers have been made with these within their transmission range (Bhar 1974) and their phase-matching properties (Bhar 1976) have been evaluated Boyd *et al* (1972) first pointed out the potentiality of the chalcopyrite crystals for the generation of FIR radiation Unlike II-VI and III-V crystals the chalocopyrite crystals are birefringent. Many of them show large enough increment in refractive index while passing through the fundamental lattice vibration frequency and therefore can give rise to phase-matched nonlinear interactions. Other established nonlinear materials are not suitable because of their poor FIR transmission. In the following we consider the generation of FIR radiation by two forms of difference-mixings : Forward-wave and backward-wave. From the measured infrared reflectivity data we evaluate seven II-IV-V_2 and seven I-III-VI_2 chalcopyrite crystals for phase-matched FIR generation.

2. Basic theory

The Far Infrared (FIR) generation of laser beams by optical mixing has received an increasing attention. It has the potential of providing a coherent tunable far infrared molecular lasers The most familiar and established technique is that of difference-frequency generation by mixing two laser beams in a non-centro-symmetric crystal. With the input pump lasers in the visible or infrared frequencies, this technique can provide a far infrared source discretely or continuously tunable for a wide range of wavelengths in the FIR beyond the reststrahlen band. The basic requirements of a nonlinear crystal, in addition to that in normal nonlinear devices for the far infrared generation are :

1) The crystal must have a good optical transmission at the operating input laser frequencies as well as at the desired generated FIR frequencies.

2) The crystal should possess sufficiently large effective optical birefringence to permit phase-matched interaction

Two types of difference frequency mixing are utilised for FIR generation. The collinear forward wave (FW) mixing technique, where the generated wave propagates in the same direction as the two driving waves, requires

$$w_P - w_i = w_s \tag{1a}$$

$$K_P - K_i = K_s. \tag{1b}$$

These equations follow from the momentum and energy conservation laws where w_s is the output generated difference frequency in the FIR. w_i and w_p are the input pump laser frequencies, and K's are the corresponding wave vectors which are related to the frequency w by the formula $K = nw/c$, n being the refractive index corresponding to the frequency w and c is the velocity of electromagnetic wave

The equations (1a) and (1b) can be written in the form

$$\frac{w_s}{w_P} = \frac{n_i - n_P}{n_i - n_s}$$

The condition for phase-matching in this FW difference down conversion process in terms of wavelength is thus

$$\frac{\lambda_s}{\lambda_P} \cdot \frac{n_i - n_P}{n_i - n_s} = 1 \tag{2}$$

where λ's denote the corresponding wavelengths. The backward wave (BW) difference frequency mixing may also be used to generate FIR radiation, where one of the waves say, the FIR generated wave w_s, is backward travelling. The requirements in this collinear BW mixing technique are

$$w_P - w_i = w_s \tag{3a}$$

$$K_P - K_i = -K_s. \tag{3b}$$

These two equations can similarly be written in the form

$$\frac{w_s}{w_P} = \frac{n_i - n_P}{n_i + n_s}.$$

The condition for phase-matching for this collinear BW mixing in relation to the wavelength is thus

$$\frac{\lambda_s}{\lambda_P}\cdot\frac{n_i-n_P}{n_i+n_s}=1. \tag{4}$$

The phase-matching conditions, equations (2) and (4), can be satisfied by proper choice of polarisation among the interacting waves in anisotropic crystals. In fact, the left hand side of each of the equations (2) and (4) can be greater than unity to accommodate e-polarisation. The variation of the corresponding extraordinary refractive index together with the frequency of one of the input pump lasers provides tuning in the generated signal wavelength λ_s. While the condition (2) in the present form for tunable FW generation is easier to realise, a careful insight into the condition for BW generation reveals that the quantity in the left hand side of equation (4) viz, $\frac{\lambda_s}{\lambda_P}\frac{B}{n'}$ must be greater than 2 so as to satisfy the phase-matching condition (where $B=n_i-n_P$ and $2n'=n_i+n_s$). This may be difficult to realise when all the interacting waves lie in the nominal transmission range of the crystal. However, when λ_s is the FIR region there is possibility of achieving the condition

The anomalous dispersion is therefore exploited for phase-matching and the available crystal birefringence is utilised for tuning purpose All crystals show a large increment in refractive index while passing through the fundamental lattice vibration frequency The refractive indices have been measured by a number of investigators for such nonlinear crystals over a wide range of wavelength from vissible to IR region. But the FIR refractive index data are not available for most of the chalcopyrite crystals We have used the lattice vibrational and reflectivity data and computed refractive index values therefrom which is discussed in the next section for the evaluation of the material in the FIR generation

We undertook a transmission and subsequent analysis to find out potential nonlinear materials including dimond like crystals (which are crystals of high nonlinearity) for the generation of tunable FIR radiation. These crystals have already been found to show good vissible-near infrared transmission As shown theoretically by Morris and Shen (1977), the FIR generation by difference frequency mixing is strongly dependent on residual absorption. This is the main reason why the FIR difference frequency generation (DFG) in crystals in most cases has been restricted to the range between 50 μm to longer wavelengths. Roughly speaking, with an absorption coefficient α, the effective length of the crystal for DFG cannot be much more than a factor $2/\alpha$. An increase in absorption coefficient increases the phase-mismatch and decreases the generated output power. The effect of absorption on FIR output power is shown as per numerical calculation of Morris and Shen (1977). In $ZnGeP_2$ (Boyd *et al* 1972) at a frequency of $w = 100$ cm^{-1}, the room temperature absorption coefficient is $\alpha = 6$ cm^{-1}. The absorption coefficient of this magnitude in a one centimeter crystal reduces the FIR output power by a factor of $\sim 0{\cdot}15$ from its corresponding no-absorption-value for a focal spot size of 25 μm of pump lasers. However, the residual absorption due to lattice band can be reduced to a very low value by cooling the nonlinear crystal to a very low temperature: while that due to free carrier to a lower minimum by compensation and cooling the sample.

3. Results and discussion

As is pointed out the detailed FIR transmission and refractive index measurements in the ternary chalcopyrite crystals are not yet available. Fortunately, quite a number of literature on the reflectivity and lattice vibrational measurement are available for several crystals We exploit such measurements for determination of FIR transmission and refractive indices. A careful study reveals that unlike the II-VI and III-V binary crystals, the ternary chalcopyrite I-III-VI$_2$ and II-IV-V$_2$ group of crystals show many reststrahlen bands. While the dominant band (Bhar 1978) determines the infrared transmission cut-off, nothing of this sort is found for the FIR region Only a few of the crystals have a wide transmission range in the FIR region On investigation, it has been observed that FIR transmission from ~ 50 μm to longer wavelengths is obtainable for $CuAlS_2$ and $CuGaS_2$ of I-III-VI$_2$ group and, $ZnSiP_2$ and $ZnSnP_2$ belonging to II-IV-V$_2$ group of crystals The transmission for e-polarisation starts at a slightly shorter wavelength than that for o-polarisation due to polarisation sensitivity of different lattice vibration modes. Such limits are shown in table 1 for phase-matched crystals. It is to be noted that for chalcopyrite crystals the transmission for e-polarisfiation is extended very near to the reststrahlen band because of narrowness of the fundamental lattice absorption band of that polarisation.

We have utilised the lattice vibrational and reflectivity data of the chalcopyrite crystals to eavluate the values of refractive index from the relation

$$n = \frac{1+R^{\frac{1}{2}}}{1-R^{\frac{1}{2}}}$$

R being the power reflection coefficient at the corresponding wavelength. Wherever possible, a scaling has been made of the FIR refractive indices with the measured (Shay and Wernick 1975) indices in the vissible region. In the majority of these crystals, the reflection coefficient is more or less constant or varies slowly at the investigated FIR frequency region. The maximum error in the measurement of reflection coefficient by different investigators has been reported to be $\pm 0{\cdot}5\%$, which results in an error in the value of refractive index to a similar figure. Although such an error in refractive indices can alter phase-matching angle in nonlinear interactions; in the present context, as we are interested only in finding suitability of the crystal for FIR generation, such an uncertainty may at most shift the limiting wavelength by few microns. It is

Table 1. FIR wavelength tuning range

Crystal	FIR transmission starting from in μm		Input Pump (μm)	Output FIR signal (μm)		References for reflectivity data
				FW	BW	
	(o)	60	1.06	45	45	
$ZnSiP_2$	(e)	30	2.36	,,	100	G. D. Holah (1972)
			5.3	,,	240	
	(o)	80	1.06	80	80	
$CdSiP_2$	(e)	150	2.36	,,	110	M. Bettini *et al*
			5.3	,,	300	(1974)
	(o)	200	.6943	50	100	
$ZnGeP_2$	(o)	33	1.06	,,	200	G. D. Holah (1974)
			2.36	,,	350	
			10.6	100	1000	
	(o)	150	2.36	75	125	
$CdGeAs_2$	(e)	60	5.3	,,	300	A. (Miller (Pvt Comn)
	(o)	35	1.06	45	200	L. B. Zlatkin *et al*
$ZnSnP_2$	(e)	35	2.360	,,	350	(1974)
$ZnSiAs_2$	(o)	90	1.06	50	250	W. H. Koschel *et al*
	(e)	50				(1974)
$CdGeP_2$	(o)	100	1.06	50	250	G D. Holah (1974)
	(e)	40				
$AgGaS_2$	(o)	100	.6328	80	80	
	(e)	60	.6943	,,	80	Van der Ziel *et al*
			1.06	,,	100	(1974)
			2.360	,,	250	
	(o)	100	.6943	100	125	
$AgGaSe_2$	(e)	80	1.06	,,	300	Miller *et al* (1976)
			2.360	,,	400	
$CuAlS_2$	(o)	50	1.06	50	150	Heneyman (1969)
	(e)	40	2.360	100	300	Koschel *et al* (1973)

to be noted that in $ZnGeP_2$ for which both FIR reflectivity and accurate refractive index data are available our method of evaluation of refractive indices predicts a phase-matching limit which agrees fairly well with that found by the measured refractive index data.

FW interaction :

For the forward wave difference-frequency mixing the two close frequency pump lasers lie within the transmission range of the crystal, while the generated difference frequency in the FIR. The most conventient pumps may be two dye lasers, two CO_2 lasers or a ruby and a ruby pumped dye laser. However other solid state lasers may also be used. Using this technique, FIR generation has been made in GaAs by Aggarwal *et al* (1973) and also in $ZnGeP_2$ by Boyd *et al* (1972). We have examined the binary crystals and found that FIR generation above $\sim 200\ \mu m$ can be made in a number of crystals of II-IV such as, ZnS, ZnSe, ZnTe, CdS, CdTe and ZnO to some extent. No material other than GaAs in group III-V has been found suitable for this type of phase-matched interaction so far

For chalcopyrite crystals (I-III-VI_2, II-IV-V_2) having a high nonlinear figure of merit, we have analysed to find that the FW interaction is permitted for FIR radiation from $\sim 50\ \mu m$ to longer wavelength for some and from $\sim 100\ \mu m$ to longer wavelength for others. The results are shown in table 1 Tuning can partly be realised by altering crystal birefringence and by noncollinear phasematching (Aggarwal *et al* 1973).

BW interaction ·

Next we explore the feasibility of backward wave difference frequency mixing for the generation of FIR radiation, wherein one of the intercacting waves is backward travelling The phase-matched BW interaction, however, requires a large effective birefringence. and because of this stringent condition, this process has so far been of limited use. By exploiting anomalous dispersion phase matching and large increment in refractive index between visible-near infrared and FIR region we have calculated to find out that crystals suitable for this purpose are only ZnSe and CdS which shows a generation from $\sim 400\ \mu m$ to longer wavelength. The other members of binary crystals are not suitable for insufficient effective birefringence.

Then comes chalcopyrite crystal family (I-III-VI_2, II-IV-V_2). The refractive index data for many chalcopyrite crystals in the vissible and infrared region are available while for FIR range, we evaluate them from the corresponding reflectivity data We have calculated the possibility of this phase-matched interaction for seven II-IV-V_2 and another seven I-III-VI_2 chalcopyrite crystals for generation of tunable FIR radiation. The results for most favourable cases are shown in table 1. In all those FW and BW calculations we have indicated in the table only the high frequency limit for each crystal and the tuning is permitted from there towards the longer wavelength side.

4. Conclusion

Seven I-III-VI_2 and seven II-IV-V_2 chalcopyrite crystals have been analysed for tunable FIR generation by nonlinear difference mixing. Their transmission ranges have been characterised. It has been found that FW interaction is possible in all these crystals while BW mixing is permitted in $ZnSiP_2$, $CdSiP_2$ and $AgGaS_2$ over an appreciable tuning range

Acknowledgment

The authors are grateful to the Department of Atomic Energy, Government of India, for financial support

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